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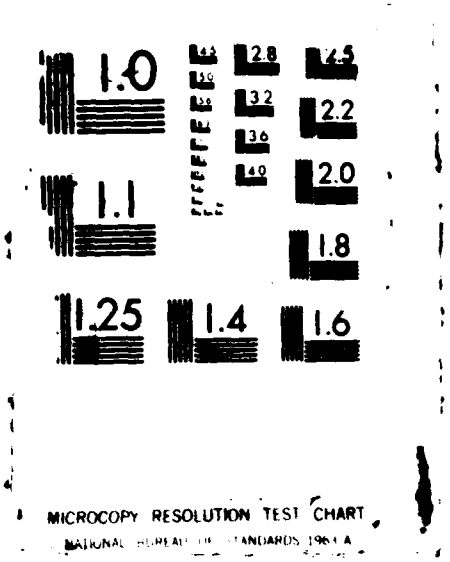
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Re-Usable Thin-Layer Spectroelectrochemical Cell for Non-Aqueous Solvent Systems

By

W. Andrew Nevin and A.B.P. Lever*

in

Analytical Chemistry

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Re-Usable Thin-Layer Spectroelectrochemical Cell for Non-Aqueous Solvent Systems

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Abstract

A thin-layer spectroelectrochemical cell for use with aqueous or organic solvent systems is described and evaluated. The cell design, comprising a working chamber formed by sandwiching Teflon spacers between two optical windows and a Teflon body, allows versatility or the working electrode material, and is easily dismantled and reassembled. Variation of the window material permits measurements to be made over a wide spectroscopic range, from the uv-visible to the infrared regions. The performance of the cell is assessed for a gold minigrid working electrode in the uv-visible region using the oxidation of [2,9,16,23-tetra(neopentoxy)-phthalocyaninato]zinc to its π-cation radical in o-dichlorobenzene, and in the infrared region by investigating the reductions of bis(2,2'-bipyridine)(2,2'-azodipyridine)ruthenium(II) bis(hexafluorophosphate) in deuterated dimethylsulfoxide.

Thin-layer spectroelectrochemistry has become a widely used technique in many laboratories for the characterisation of the redox and spectroscopic properties of electroactive species [1]. Many different designs of optically transparent thin-layer electrochemical cells have been reported, based on a variety of working electrode materials, such as gold minigrid, platinum gauze, vitreous carbon, metal foam, tin oxide and thin metal or carbon films. Relatively simple cell designs have been used successfully with aqueous solutions; however, difficulties arise with organic solvents, since these attack the adhesives commonly used in cell construction, so that cell lifetime is severely limited. As a result, most cells designed for use with organic solvents have consisted of complex assemblies, with inconvenient construction and in which cleaning or replacement of the working electrode is often difficult, particularly with the fragile gold minigrid (2-6). An improved cell has recently been reported by Lin and Kadish (6) which shows excellent electrochemical behaviour; however, it requires a fairly robust platinum gauze working electrode. As yet, no design has been reported for organic solvents which allows convenient assembly, cleaning and versatility of working electrode material.

We report here a re-usable OTTLE cell in which a gold minigrid working electrode is sandwiched between Teflon spacers and a Teflon body without the use of epoxies or other adhesive materials. Leakage is not a problem over the normal experimental time periods. The cell is easily dismantled for cleaning or replacement of the gold minigrid and rapidly reassembled. It can be used under degassed conditions with aqueous solution or a variety of common organic electrochemical solvents, such as o-dichlorobenzene, N,N-dimethylformamide, propylene carbonate and dimethylsulphoxide. A useful feature of the cell is that

versatility over a wide spectroscopic range by varying the window material (eg. from the uv-visible-near ir (quartz, pyrex) to the infrared regions (NaCl, CaF2, CsI). Little use has been made of OTTLEs in the infrared region but interest appears to have been growing recently [3,14].

The use of the cell in the uv-visible region is illustrated by the oxidation of [2,9,16,23-tetra(neopentoxy)phthalocyaninato]zinc (ZnTNPc[-2]) in o-dichlorobenzene, and in the infrared region by the reduction of [bis(2,2'-bipyridine)(2,2'-azodipyridine)ruthenium(II) bis(hexafluorophosphate) ([Ru(bpy)2(Azdpy)](PF6)2) in deuterated dimethylsulfoxide.

Experimental Section

Cell Construction

The design of the thin-layer cell is shown in Figure 1. The working chamber is formed by sandwiching two Teflon spacers between two windows, and contains a semi-transparent gold minigrid (500 wires/inch, 60% transmittance, Buckbee Mears Co., St. Paul, MN) as the working electrode, platinum foil as the counter, and silver foil (Aldrich, 0.025 mm thick) or AgCl coated silver foil as the reference electrode. This last was prepared electrochemically by passing an anodic current of ca. 15 $\mu A/cm^2$ for 30 min through the silver foil immersed in 0.1 M HCl (15). The pure silver foil reference will drift up to 100mV which can be an inconvenience. The AgCl coated foil is much more stable, and is preferred, especially if the solution can tolerate chloride ion as the supporting electrolyte anion.

The counter and reference electrodes are separated from each other and from the working electrode by two rolls of Teflon tape. The assembly is held between two Teflon holders which are tightened together to give a pressure seal between the Teflon spacers and windows. The dimensions of

the working chamber are defined by the size and thickness of the Teflon spacers. In this study the cell thickness was 0.45 mm, with a chamber volume of 100 ul. Electrical contact to the gold minigrid is made outside the working chamber by attaching a tinned copper wire with molten indium metal using a soldering technique. Contacts to the counter and reference electrodes are made using microgator clips. Further information on the cell design may be obtained from the Authors.

The cell is filled via hypodermic needles inserted between the Teflon spacers, and in order to eliminate oxygen, cell filling may be carried out under an inert atmosphere using degassed solutions. An assembled cell can usually be used for several experiments, by cleaning each time with a suitable solvent, via the hypodermic needles.

Materials

ZnTNPc(-2) (16) and $Ru(bpy)_2(Azdpy)(PF_6)_2$ (17) were prepared as described elsewhere. o-Dichlorobenzene (DCB; Aldrich, Gold Label) and deuterated dimethylsulfoxide (DMSO-d_6; MSD Isotopes) were used as supplied. Tetrabutylammonium perchlorate (TBAP; Kodak) was recrystallised from absolute ethanol and dried in a vacuum oven at 50°C for 2 days. Lithium chloride (Anachemia, reagent grade) was dried at 120°C for 24 h. Water was purified by double distillation over $KMnO_4$, followed by passage through a Barnstead organic removal cartridge and two Barnstead mixed resin Ultrapure cartridges. All other chemicals used were of analytical grade.

Methods

Electronic spectra were recorded with a Hitachi Perkin-Elmer Microprocessor Model 340 spectrometer. Infrared spectra were recorded using a Nicolet Model SX20 Fourier Transform Infrared (FTIR) spectrometer.

A gain of 16 and 64 scans per spectrum were used for the FTIR measurements. Electrochemical measurements were made with a Princeton Applied Research (PAR) Model 174A polarographic analyzer coupled to a PAR Model 175 universal programmer. The thin-layer cell was filled under an atmosphere of nitrogen in a Vacuum Atmospheres Drilab (organic solutions) or a glove bag (aqueous solutions). DMSO-d6 solutions were prepared in the dry box. DCB solutions were prepared in air, degassed by repeated freeze-pump-thaw cycles, and then transferred to the dry box. Aqueous solutions were degassed by purging with nitrogen gas.

The optical window material may be varied according to the spectroscopic range required. In this study, Pyrex windows were used for the uv-visible region, and sodium chloride windows for the infrared measurements.

Results and Discussion

The electrochemical characteristics of the cell were assessed for aqueous solution using the $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ couple in 1 M KNO_3 solution, as shown in Figure 2. The cyclic voltammetric waves are almost symmetrical, and the current returns approximately to the baseline after each peak maximum, indicating that the cell closely follows the expected ideal thin-layer behaviour (18), and that edge effects are small. Some effects of the resistance of the thin solution layer are observed, as evidenced by an increase in peak to peak separation with increasing scan rate from 15 mV at 1mV/s to 100 mV at 100 mV/s. Peak to peak separations measured at several scan rates are given in Table 1.

Organic solutions give a greater deviation from ideal behaviour. Peak to peak separations are larger than for aqueous solution, reflecting a higher iR drop across the thin layer. Figures 3 and 4 show the results

obtained for the first oxidation of ZnTNPc(-2) to its π-cation radical, [ZnTNPc(-1)]+, in DCB solution with 0.3 M TBAP as supporting electrolyte. The cyclic voltammogram (Fig. 3) shows well defined fairly symmetrical waves, having a peak to peak separation of 240 mV at a scan rate of 1 mV/s. Figure 4 shows the formation of the π-cation radical species upon oxidation across this couple. The final spectrum is very similar to those recently reported (19) for the electrochemical and photochemical oxidation of the unsubstituted zinc phthalocyanine derivatives, ZnPc(im) (im = imidazole) and ZnPc(py) (py = pyridine), respectively, in dichloromethane solution. The spectroscopic changes are fully reversible to the initial species upon re-reduction. Time for equilibrium at each potential is ca. 15 min in DCB solution; however, in more conducting solvents such as N,N-dimethylformamide, equilibrium is reached within 5 min.

The OTTLE cell can easily be adapted for the infrared region by using NaCl or another suitable window material, and by choosing a solvent/electrolyte combination whose absorption is low in the region of interest for the compound under investigation. Use of the FTIR technique enables one to subtract out the solvent/electrolyte absorption from the sample solution to leave the pure sample spectrum.

As an example, we report the reduction of $Ru(bpy)_2(Azdpy)(PF_6)_2$ in DMSO-d6 with LiCl as supporting electrolyte. This solvent/electrolyte combination gives a spectroscopic window in the region of 1100 - 1700 cm^{-1}, where important infrared bands of this complex occur. Spectra were obtained by subtraction of the spectrum of a 'blank' solution of LiCl in DMSO-d6 in the OTTLE cell taken through the gold minigrid, from that containing the sample. The subtracted spectrum of the sample in solution was found to be almost identical to that measured in a KBr disc, with little shifting of the band frequencies. Table II lists the frequencies

of the main absorptions in the region of 1200 - 1600 cm^{-1}. The principal features (17) are the occurrence of a strong band at 1334 cm^{-1} due to the azo N=N stretching mode, and several strong overlapping bands in the regions of 1430 - 1500 cm^{-1} and 1560 - 1600 cm^{-1}, assigned to azopyridine ring and bipyridine modes. A shoulder at 1317 cm^{-1} is also associated with the azo group, and is probably an (Naz-C) mode (17,20). The cyclic voltammogram (17) of $Ru(bpy)_2(Azdpy)(PF_6)_2$ in DMSO/LiCl shows two reversible one-electron reductions, at -0.76 V and -1.29 V versus the ferrocenium/ferrocene couple, corresponding to the consecutive addition of electrons to the azo N=N bond (17,21).

Figures 5(a) and 5(b) show the spectroscopic changes observed on reduction of a solution of 0.011 M $Ru(bpy)_2(Azdpy)(PF_6)_2$ in DMSO-d_6 with 0.09 M LiCl, across the first and second reduction couples, respectively. The main bands of the reduction products are given in Table II. Reduction across the first reduction wave results in several changes in the peaks between 1400 and 1600 cm^{-1}. The band at 1605 cm^{-1} shows a large decrease in intensity, while small shifts of 3-5 cm^{-1} to lower energy are seen for the bands at 1583 and 1568 cm^{-1}. In the region of 1400 cm^{-1}, the 1467 and 1447 cm^{-1} bands disappear, while new bands appear at 1457 and 1418 cm^{-1}. Change in specific bands, however, are difficult to follow due to the overlapping nature of the azopyridine and bipyridine absorptions. The band assigned to the azo group shows a reduction in intensity relative to those at 1400 cm^{-1}, and is shifted by 20 cm^{-1} to lower energy, consistent with the addition of an electron to the N=N bond (17,21). On forming the second reduction product, the azo peak at 1304 cm^{-1} disappears and a single relatively more intense band appears to lower energy, at 1295 cm^{-1}. Several changes also occur in the region of 1400-1600 cm^{-1} as shown in Fig. 5(b), notably a merging of the bands near 1600 cm^{-1} into one broad

multiple band at 1602 cm^{-1}. These spectroscopic changes are reversible upon re-oxidation to the initial species.

The results reported here have been obtained using a gold minigrid working electrode. However, an attractive feature of the cell is that many other electrode materials can be easily incorporated. We have obtained satisfactory spectroelectrochemical performance using windows coated with a conducting layer of tin oxide or thin carbon film as the working electrode. Similarly, the cell may readily be used with semi-transparent metal film electrodes, or other electrode materials, such as platinum gauze.

In summary, the thin-layer cell described here has several advantages over many previous cell designs. These include versatility of the spectroscopic range and electrode material, good electrochemical behaviour, ease of cleaning and assembly, and suitability for use with aqueous or organic solutions. In particular, the cell allows the convenient and rapid acquisition of infrared data on redox species, an area which has been neglected in the past, but which can provide important information concerning the nature of the redox species and the electrochemical processes taking place.

No problems were experienced in recording the spectra of air sensitive materials even though there is evidence that Teflon is somewhat permeable to oxygen. Where extreme air sensitivity is a problem, Kel-F might be used for the spacer material.

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Figure Legends

Figure 1. Schematic diagram of the thin-layer spectroelectrochemical cell: (a) front view; (b) side view; (c) assembly of the cell.

Figure 2. Thin-layer cyclic voltammograms of 1 mM $K_3Fe(CN)_6$ in 1 M KNO_3, recorded at potential scan rates of (a) 100 mV/s (__), and (b) 1mV/s (----). The reference electrode is AgCl-coated Ag foil.

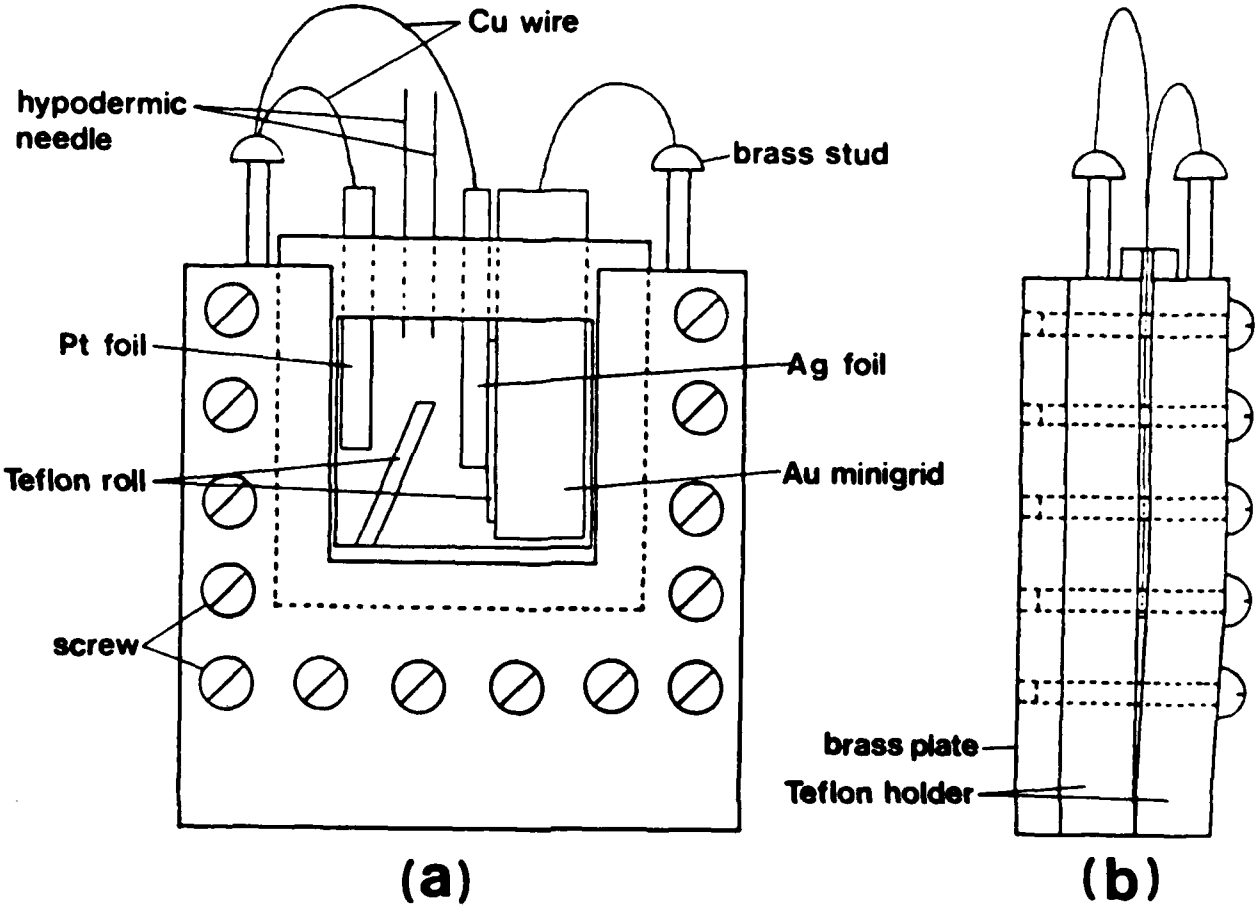
Figure 3. Thin-layer cyclic voltammogram of 4.5×10^{-4} M ZnTNPc in DCB with 0.3 M TBAP. Scan rate = 1 mV/s. The reference electrode is AgCl-coated Ag foil.

Figure 4. Development of the thin-layer spectra with time for the oxidation of 1.6×10^{-4} M ZnTNPc(-2) in DCB with 0.3 M TBAP. The reference electrode is Ag foil. Reading from the top spectrum down, the percentage of un-oxidised material is 100, 95, 69, 56, 39, 21, 12, 6, 2, 0%. The experiment is complete in about 15 minutes.

Figure 5. Development of the thin-layer FTIR spectra with time for the reduction of 0.011 M $Ru(bpy)_2(Azdpy)(PF_6)_2$ in DMSO-d_6 with 0.09 M LiCl: (a) first reduction; Reading from the top spectrum down, the percentage of un-reduced material is 100, 71, 54, 34, 0%. (b) second reduction. The reference electrode is Ag foil. THe experiment is complete in about 15 minutes.

Table I. Peak to Peak Separations (E) of the $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ Couple in 1 M KNO_3 Solution.

Scan rate (mV/s)	1	10	20	50	100
E (mV)	15	20	25	45	100


Cu wire
hypodermic needle
brass stud
Pt foil
Ag foil
Teflon roll
Au minigrid
screw
brass plate
Teflon holder
(a)
(b)

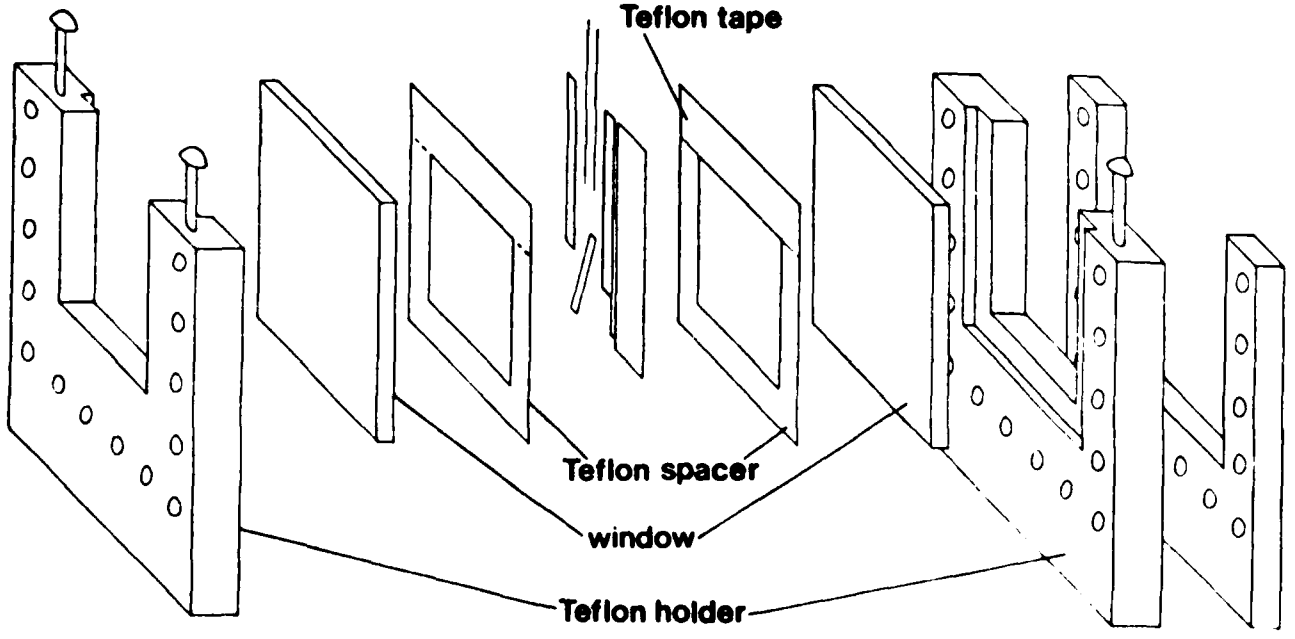
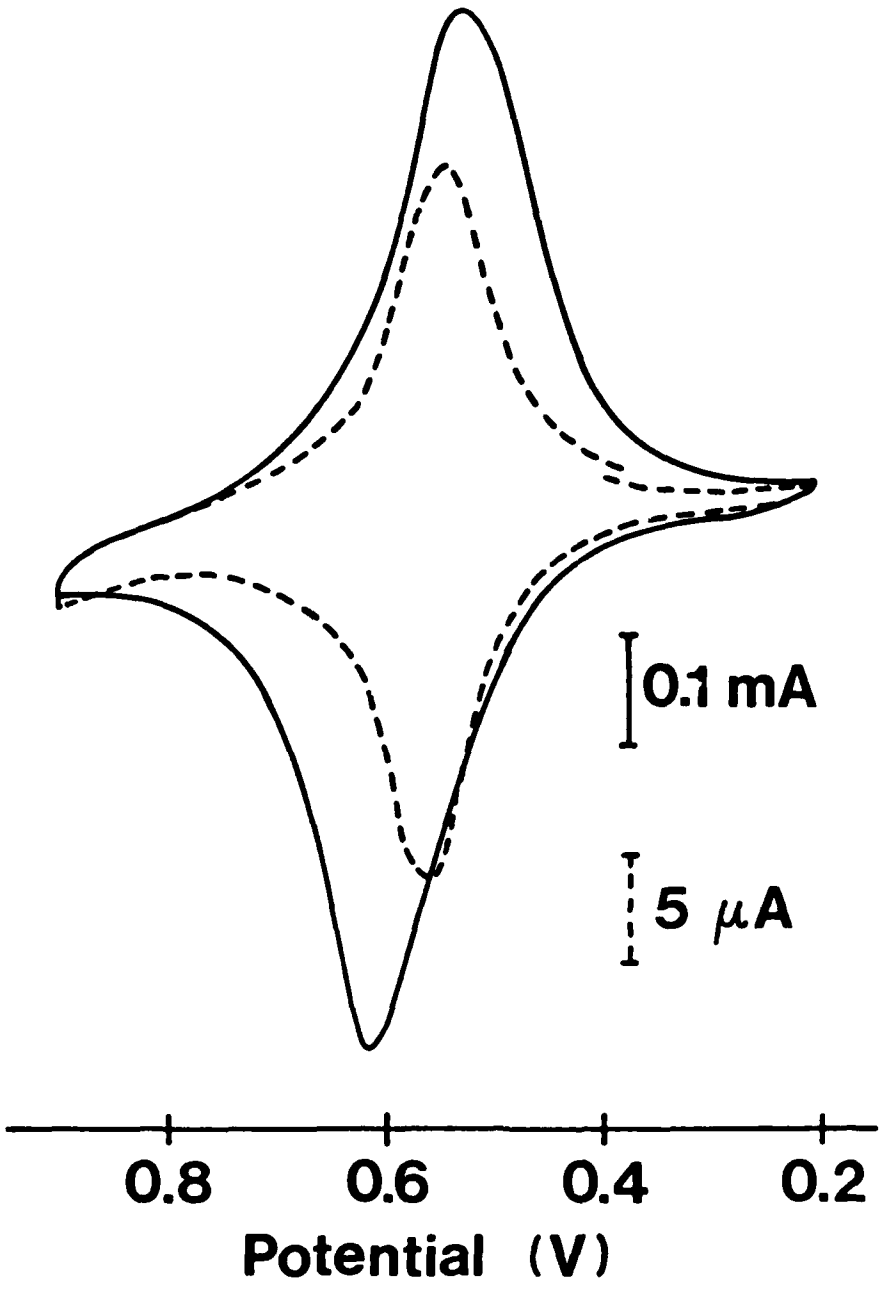
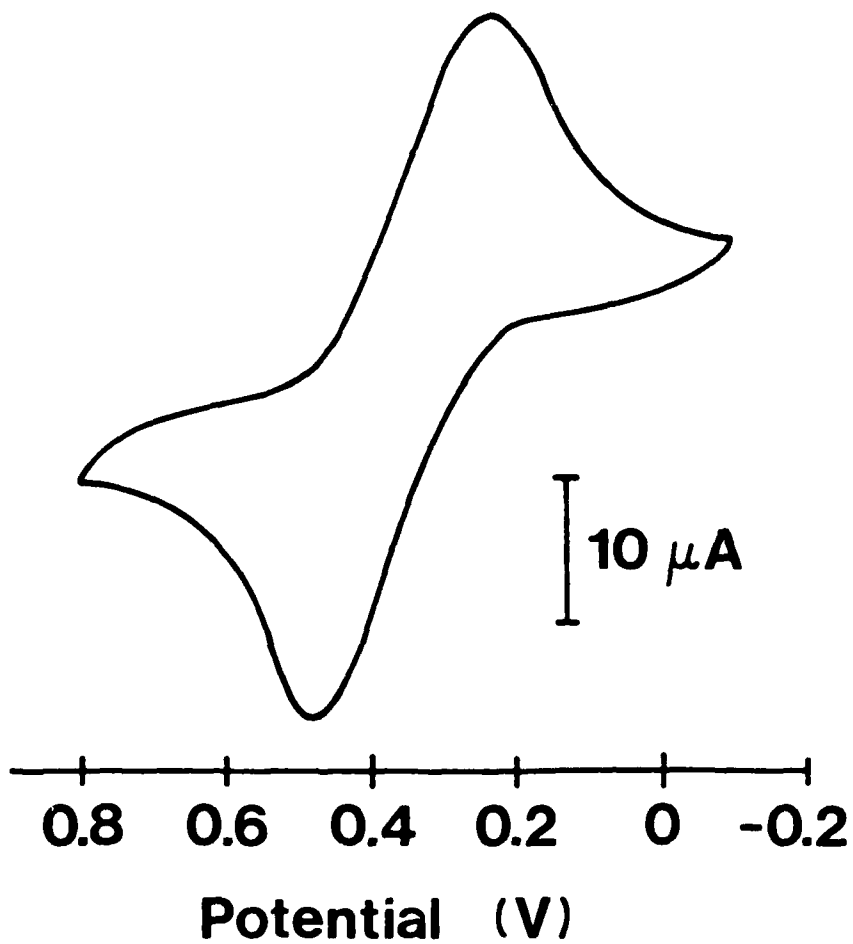
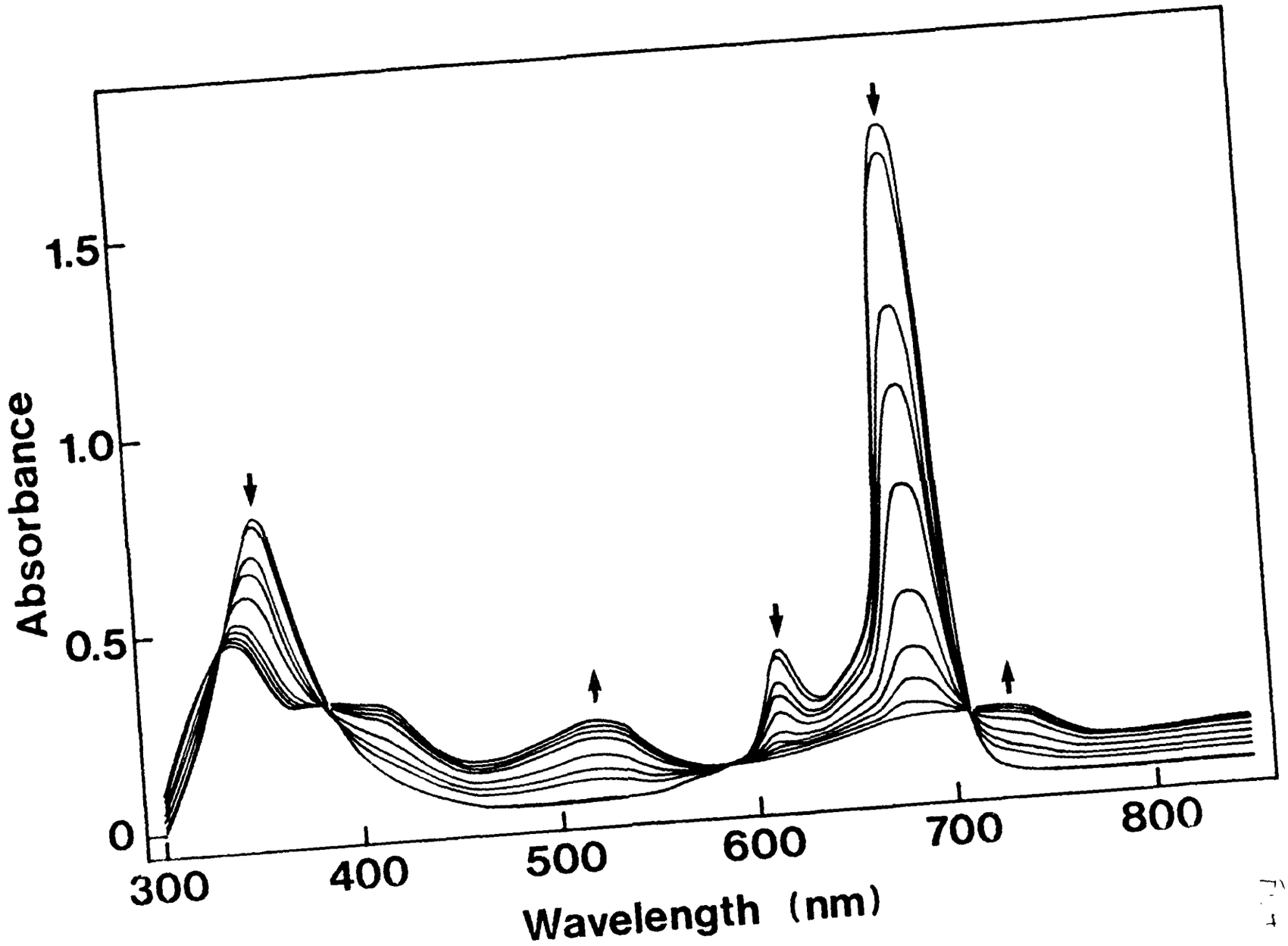
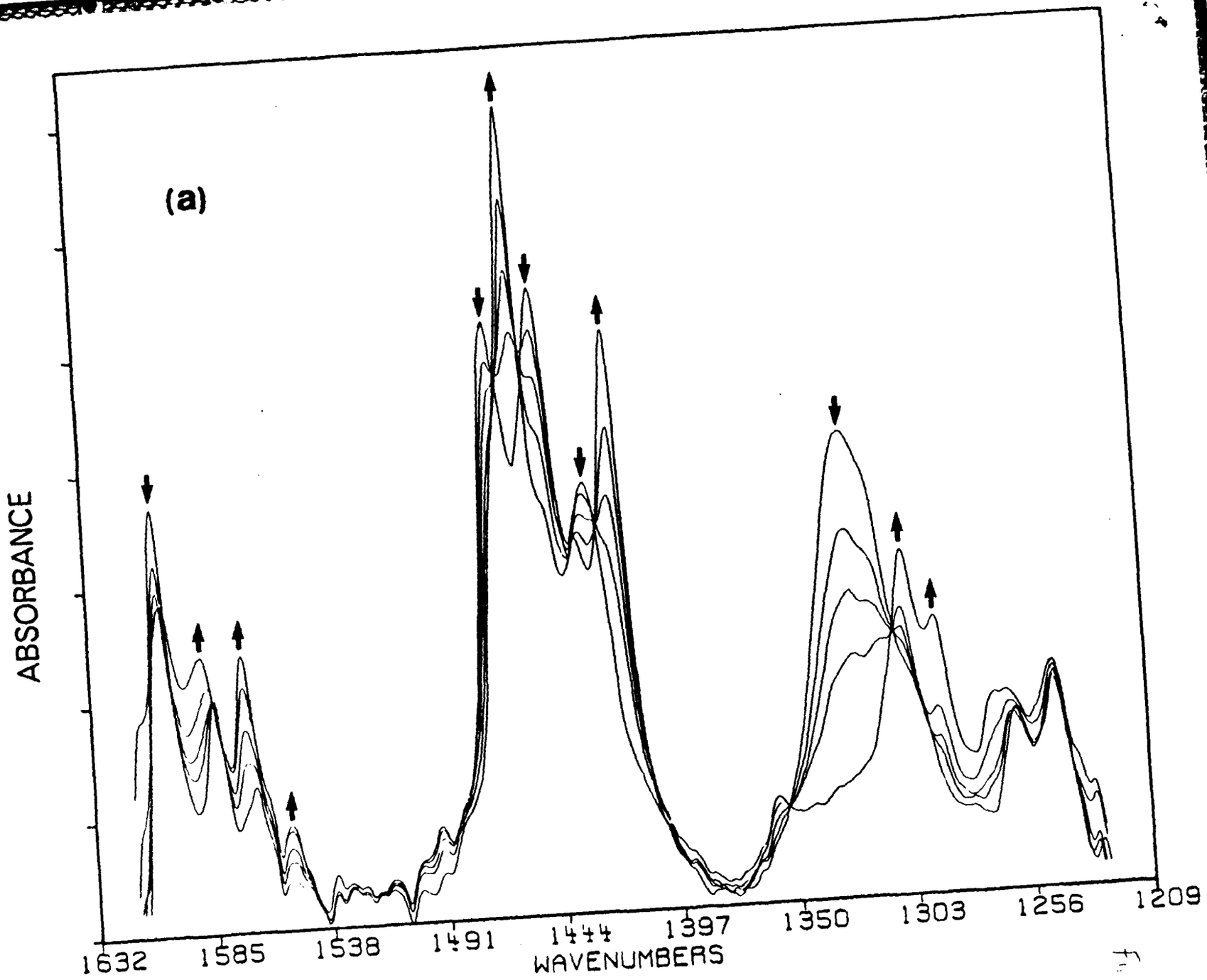

Teflon tape
Teflon spacer
window
Teflon holder
(c)

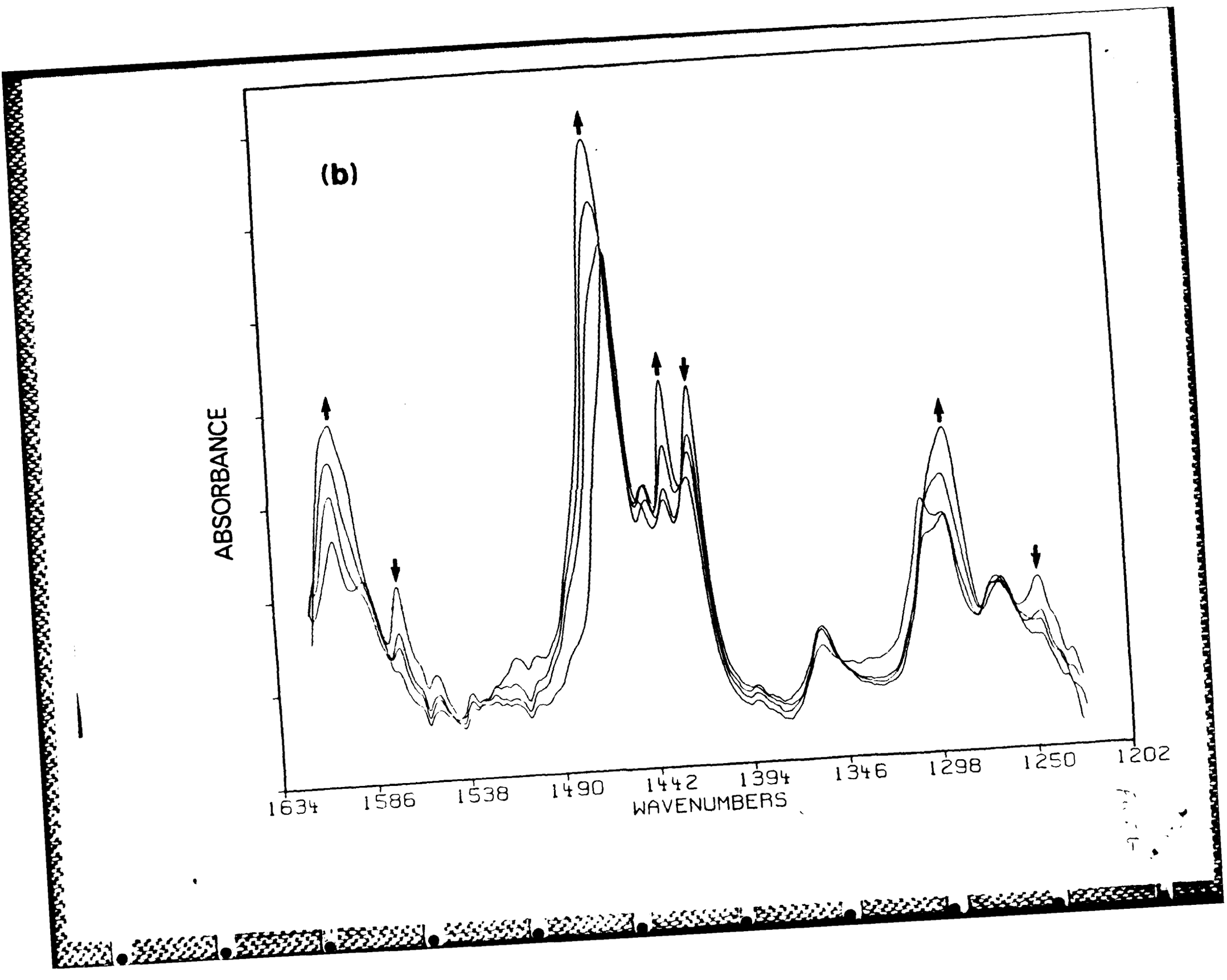
Fig 2




10 μA
0.8
0.6
0.4
0.2
0
-0.2
Potential (V)


Absorbance
1.5
1.0
0.5
0
300
400
500
600
700
800
Wavelength (nm)


(a)
ABSORBANCE
1632
1585
1538
1491
1444
1397
1350
1303
1256
1209
WAVENUMBERS


(b)
ABSORBANCE
1634
1586
1538
1490
1442
1394
1346
1298
1250
1202
WAVENUMBERS

END

DATE

FILMED

JAN

1988